



Novel anti-flooding poly(dimethylsiloxane) (PDMS) catalyst binder for microbial fuel cell cathodes

Fang Zhang^a, Guang Chen^{a,b}, Michael A. Hickner^b, Bruce E. Logan^{a,*}

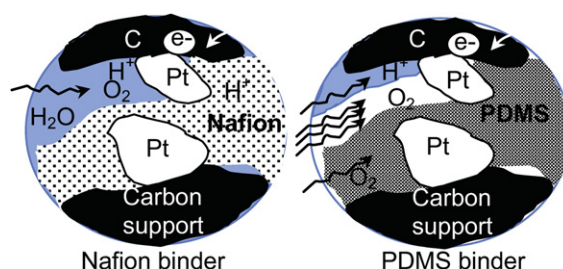
^a Department of Civil and Environmental Engineering, Penn State University, 212 Sackett Building, University Park, PA 16802, USA

^b Department of Materials Science and Engineering, Penn State University, 310 Steidle Building, University Park, PA 16802, USA

HIGHLIGHTS

- Poly(dimethylsiloxane) (PDMS) was tested as a catalyst binder in a microbial fuel cell.
- PDMS cathodes produced comparable power and improved stability compared to Nafion.
- The hydrophobicity of PDMS improved oxygen mass transfer to the catalyst sites.
- The cost of PDMS is only 0.23% that of Nafion.

GRAPHICAL ABSTRACT



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ABSTRACT

Poly(dimethylsiloxane) (PDMS) was investigated as an alternative to Nafion as an air cathode catalyst binder in microbial fuel cells (MFCs). Cathodes were constructed around either stainless steel (SS) mesh or copper mesh using PDMS as both catalyst binder and diffusion layer, and compared to cathodes of the same structure having a Nafion binder. With PDMS binder, copper mesh cathodes produced a maximum power of $1710 \pm 1 \text{ mW m}^{-2}$, while SS mesh had a slightly lower power of $1680 \pm 12 \text{ mW m}^{-2}$, with both values comparable to those obtained with Nafion binder. Cathodes with PDMS binder had stable power production of $1510 \pm 22 \text{ mW m}^{-2}$ (copper) and $1480 \pm 56 \text{ mW m}^{-2}$ (SS) over 15 days at cycle 15, compared to a 40% decrease in power with the Nafion binder. Cathodes with the PDMS binder had lower total cathode impedance than those with Nafion. This is due to a large decrease in diffusion resistance, because hydrophobic PDMS effectively prevented catalyst sites from filling up with water, improving oxygen mass transfer. The cost of PDMS is only 0.23% of that of Nafion. These results showed that PDMS is a very effective and low-cost alternative to Nafion binder that will be useful for large scale construction of these cathodes for MFC applications.

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1. Introduction

Microbial fuel cell (MFC) based technologies have attracted considerable attention as a method to extract bioelectricity from biomass, especially from organic matter and pollutants in wastewater [1–5]. In a MFC bacteria oxidize organic or inorganic matter and donate electrons to the anode to generate current [3,4]. Air cathode MFCs are the most promising configuration for

applications involving wastewater treatment, due to their electrical power output, simple structure of the reactors, and the lack of a need for aerating the wastewater. However, oxygen reduction at the cathode is limited by poor kinetics under MFC typical operating conditions (ambient temperature and neutral pH), and mass transport limitations due to diffusion of oxygen through the cathode porous structure, the low solubility and diffusivity of oxygen in water, and accumulation of inert gas in the pores [6,7]. As a result, the cathode is usually the limiting factor in power production in most MFCs [8–10]. Cathode performance and its limited surface area have therefore been found to be two of the

* Corresponding author. Tel.: +1 814 863 7908.

E-mail address: blogan@psu.edu (B.E. Logan).

main challenges for scaling up MFCs for wastewater treatment applications [11].

Nafion has been used as a standard catalyst binder polymer for MFCs, due to its high proton conductivity. Efforts have been made to find alternatives to Nafion, because it is a very expensive polymer which costs \$667 per m². Low-cost hydrophobic polytetrafluoroethylene (PTFE) has been tested as the binder in several studies [12,13]. Replacing Nafion with PTFE in a MFC decreased power generation from $480 \pm 20 \text{ mW m}^{-2}$ to $360 \pm 10 \text{ mW m}^{-2}$, although the PTFE binder showed less degradation in performance over time [12]. Mixtures of PTFE and Nafion have been examined, and power decreased as the amount of PTFE was increased in the binder mixture. With only the PTFE binder, the maximum power was 549 mW m^{-2} , compared to 1060 mW m^{-2} obtained using only Nafion [13]. Comparison of sulfonated and non-sulfonated poly(sulfone) showed that the non-ionic binder had better electrochemical performance and the lowest charge transfer resistance, suggesting that the ionic binder resulted in ionic gradients that impeded proton transfer [14]. The ionic binder had the highest initial power of 1660 mW m^{-2} in the second cycle, but the non-sulfonated poly(sulfone) (Radel) produced the most power (1200 mW m^{-2} , with 100 mM phosphate buffer) after 22 cycles, and it was the best in terms of long-term stability. Further tests with hydrophilic polymers have shown that non-ionic polymers, with greater water uptake, increased the accessible surface area for oxygen reduction and thus increased the performance [15]. Although these alternative binders all initially had a lower power production than Nafion, performance of the best materials became nearly equivalent to Nafion in longer term tests [14,15].

Water flooding is a significant negative factor for cathode performance in fuel cell studies as it reduces oxygen transfer to the reaction sites in the cathode. Water flooding within the catalyst layer, or in the diffusion layer, can result in a non-uniform distribution of reactant over the active catalyst area [16]. Flooding reduces cathode performance in two separate ways: by covering electrochemically active sites with liquid water, and by hindering oxygen transport to the reaction sites [8]. In air cathode MFCs, cathodes have one side facing the solution and the other side facing air, with the cathode catalyst directly in contact with liquid water. Compared to polymer electrolyte membrane (PEM) fuel cell operation conditions, MFCs operate at much lower temperatures with passive air flow, and any product water would be more likely to condense to liquid water and thus would not be easily removed by convection on the air side. These disadvantages could result in water flooding problems in MFCs, but this issue has not been well addressed in these systems.

Most strategies for mitigating water flooding in fuel cells are based on introducing hydrophobic materials into the cathode structure, for example by applying a hydrophobic diffusion layer to the air-side of the cathode, or using a micro-porous layer [17,18]. Wet proofing using polytetrafluoroethylene (PTFE) was shown to increase the performance of nickel foam cathodes in MFCs, likely through the inhibition of nickel corrosion and reduction in cathode flooding [19]. An anti-flooding cathode catalyst layer was developed for a PEM fuel cell by adding dimethyl silicone oil into the catalyst layer with a Nafion binder, which increased hydrophobicity and more effectively expelled water out of the voids of the catalyst layer, and increased power [20]. These studies showed that creating more hydrophobic conditions can be beneficial for power production by mitigating water flooding at the cathode catalyst layer.

The hydrophobic polymer poly(dimethylsiloxane) (PDMS) was examined here as a novel anti-flooding catalyst binder for MFC cathodes because it is also highly permeable to oxygen. Unlike Nafion, PDMS is not ionically conductive. PDMS is an inexpensive polymer, which has previously been used to make diffusion layers

on the air-side of MFC cathode to prevent water leakage, because it is easy to apply with a low curing temperature [17,21]. In order to examine the usefulness of PDMS as a catalyst binder, cathodes were constructed around stainless steel (SS) or copper mesh, with a PDMS binder for the catalyst layer on the solution-side. Copper mesh was compared to SS mesh due to its high electrical conductivity, which could benefit increased power production. Cathodes were made using 50-mesh materials, which were previously shown to have high power production among a series of different sized mesh [21]. These cathodes were compared to cathodes made with the same materials except for the use of a Nafion binder. Cathodes were tested in MFCs for 15 cycles using pre-acclimated anodes to examine the effect of the binder and mesh materials on power production, cathode potentials, and coulombic recoveries. Cathodes were also characterized abiotically using galvanostatic polarization and electrochemical impedance spectroscopy in an electrochemical cell.

2. Experimental

2.1. Cathodes

Cathodes were constructed around 50×50 mesh (mesh opening size of 0.28 mm and wire diameter of 0.23 mm) as previously described [21], except that PDMS was used as the catalyst binder, with either SS (Type 304) or copper mesh (McMaster-Carr, OH). For the catalyst layer, 5 wt% PDMS was used as the binder with 0.5 mg cm^{-2} Pt (treatment), and compared to cathodes made with Nafion binder ($33.3 \mu\text{L cm}^{-2}$ of 5 wt% Nafion solution) (control). PDMS was prepared using a 10:1 mixture of SYLGARD 184 silicone elastomer base and SYLGARD 184 silicone elastomer curing agent (Dow Corning, MI), that was further diluted to 5 wt% with toluene [17]. To avoid inactivating the Pt catalyst at high temperatures, the PDMS binder was cured at room temperature for at least two days before being used. Two layers of PDMS/carbon black were also on the air-facing side as the diffusion layer to prevent water leakage through the cathode as previously described [17].

2.2. MFC construction and operation

MFCs were single-chamber cubic-shaped reactors with an anode chamber 4 cm long and 3 cm in diameter [22]. The anodes were graphite fiber brushes that were heat treated at 450°C for 30 min and inoculated with a pre-acclimated cell suspension from an existing MFC [23,24]. MFCs were fully acclimated and operated in fed-batch mode using carbon cloth cathodes with a Pt catalyst at 30°C before changing to the metal mesh cathodes. The medium contained 1 g L^{-1} sodium acetate dissolved in 50 mM phosphorus buffer (Na_2HPO_4 , 4.58 g L^{-1} ; $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$, 2.45 g L^{-1} ; NH_4Cl , 0.31 g L^{-1} ; KCl , 0.13 g L^{-1} ; trace minerals and vitamins; conductivity of 6.95 mS cm^{-1}). The external resistance was set at the resistance which produced the maximum power in polarization tests at cycle 1 and cycle 6: 50Ω for cathodes with PDMS binder, and 75Ω for cathodes with Nafion binder (except during cycle 2 to 5, where cathodes with copper mesh and Nafion binder were set at 50Ω). All reactors were operated in duplicate at 30°C .

2.3. Calculations and measurements

Voltage (E) across the external resistor in the MFC circuit was measured at 20 min intervals using a data acquisition system (2700, Keithley Instrument, OH) connected to a personal computer. Current ($I = E/R$) and power ($P = IE$) were normalized by the projected surface area of the cathode (7 cm^2). Polarization tests were

performed using the single-cycle method at the first cycle and cycle 6 by varying the external circuit resistances from 1000 to 20 Ω in decreasing order (20 min per resistance). Coulombic recoveries were calculated as the ratio of recovered coulombs to the theoretical amount of coulombs that can be produced from acetate oxidation [1].

2.4. Electrochemical tests

Cathodes were characterized using galvanostatic polarization and electrochemical impedance spectroscopy (EIS) with a potentiostat (PC4/750, Gamry Instruments) in an abiotic electrochemical cell. The electrochemical cell consists of a working electrode (air cathode with 7 cm² projected surface area), a Ag/AgCl reference electrode (Bioanalytical Systems, Inc., RE-5B; +0.211 V versus a standard hydrogen electrode, SHE) and a Pt mesh counter electrode [17]. The cathode in this electrochemical cell was identical to that in the MFC, with the solution present on the catalyst side of the cathode and air on the other side. Galvanostatic polarization was performed immediately after putting the cathode into the electrochemical cell, and repeated one day later to characterize the change of cathode performance due to water flooding. In galvanostatic polarization tests a different current was set (0 to –10 mA, in 0.5 mA increments) for 30 min for the first four points, and at 15 min intervals thereafter. Current was then normalized by the cathode surface area and current density was plotted as a function of the steady state potential.

EIS tests were performed after the galvanostatic polarization tests. Impedance measurements were conducted at polarized conditions of 0.2 V, 0.1 V and 0 V (vs SHE), which were potentials similar to the MFC cathode operating potentials, over a frequency range of 100 kHz to 1 mHz with a sinusoidal perturbation of 10 mV amplitude. Spectra were fitted to an equivalent circuit as previously described [21] to obtain the solution resistance R_s , charge transfer resistance R_{ct} , and diffusion resistance R_d .

3. Results and discussion

3.1. Power production of cathodes using different binders

Cathodes were examined in MFCs for their power production with pre-acclimated anodes that produced stable power before the mesh cathodes were used. Polarization tests taken at cycle 1 and cycle 6 showed that the anode performance was identical among reactors with different cathodes and at different cycles (Fig. 1C and D), and therefore changes in power over time were due to differences in cathode performance. With a PDMS binder, copper and SS mesh cathodes resulted in similar performance. Cathodes with the PDMS binder initially had poorer performance, with a maximum power production of 1260 ± 51 mW m⁻² with copper mesh, and a similar power of 1210 ± 33 mW m⁻² with SS mesh (Fig. 1A and C). This low power production was assumed to be due to inhibition of proton transfer produced by a low water content, which would have resulted from using a material like PDMS that has a high hydrophobicity. When the cathodes became better wetted with water produced from the current over time, the proton transfer to the active sites was improved, cathode potentials increased (Fig. 1C and D), and power increased to 1710 ± 1 mW m⁻² (cycle 4) with copper mesh, and to 1680 ± 12 mW m⁻² with SS mesh (cycle 7). Power production after this time decreased by ca. 12% to 1510 ± 22 mW m⁻² with copper mesh and 1480 ± 56 mW m⁻² with SS mesh at cycle 15 (Fig. 2), likely due to the biofouling of the cathode surface.

With Nafion binder, high power densities were initially produced, with 2220 ± 34 mW m⁻² using copper mesh and 1840 ± 17 mW m⁻² with SS mesh (Fig. 1A and C). Copper mesh had better performance than SS mesh when using the Nafion binder, most likely due to a higher electrical conductivity of copper which decreased charge transfer resistance (see below). After several cycles the advantage of Nafion disappeared, which could be a result of several factors, including biofouling. This change in power was

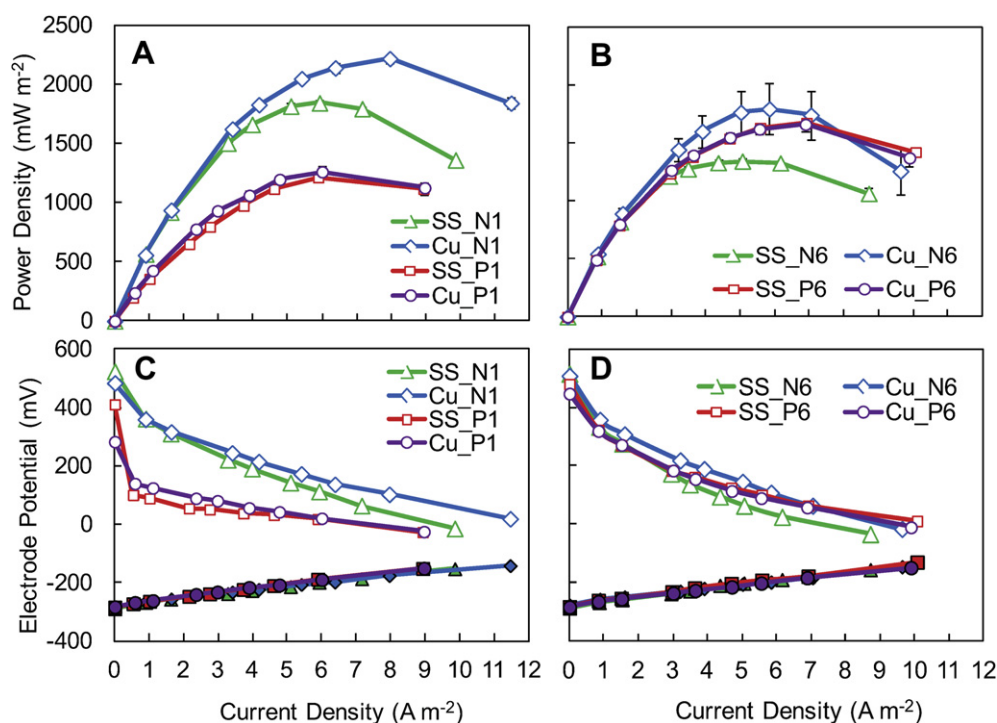


Fig. 1. Power density curves at (A) the first cycle and (B) cycle 6, and electrode potentials (solid symbols for anode potentials and open symbols for cathode potentials) at (C) the first cycle and (D) cycle 6, with stainless steel (SS) or copper (Cu) mesh cathodes using PDMS binder compared to Nafion binder.

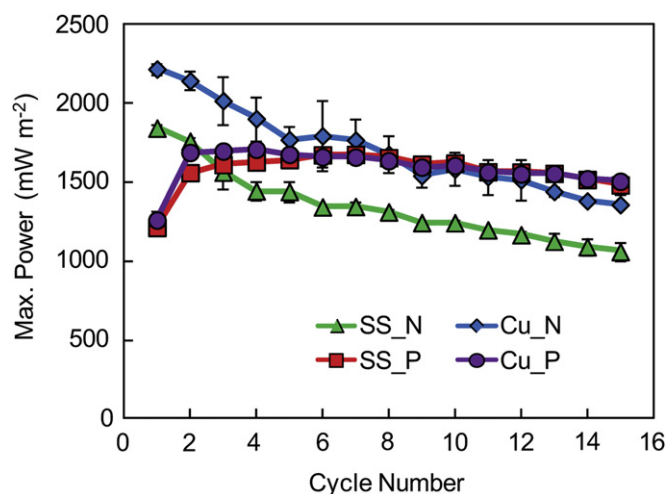


Fig. 2. Maximum power production over cycles with cathodes built around either stainless steel or copper mesh, with PDMS or Nafion binder (Data for cycle 1 and cycle 6 obtained from polarization tests, rest data obtained by setting external resistor at the resistance where maximum power was obtained in the polarization tests.).

reflected by decreased cathode potentials from cycles 1 to 6 (Fig. 1C and D). The maximum power continuously decreased over time, reaching $1360 \pm 3 \text{ mW m}^{-2}$ for the copper mesh and $1060 \pm 54 \text{ mW m}^{-2}$ with the SS mesh at cycle 15 with the Nafion binder. These final values were 28% lower than those produced with the PDMS binder with SS mesh, and 10% lower than those with copper mesh (Fig. 2). Decreases in cathode performance over time with Nafion have previously been reported in several studies [12,14,15,25]. Therefore, while power densities were initially larger with a Nafion binder, the MFCs with the PDMS binder in the cathode produced more stable maximum power than those with Nafion over time, achieving higher power production after several cycles. The reduced performance degradation with PDMS binder might be due in some part to its anti-fouling properties introduced by its hydrophobic surface, making it less prone to performance degradation over time compared to Nafion.

The power achieved here using PDMS binder in the cathodes was the highest among studies investigating alternatives to a Nafion binder. In these previous studies carbon cloth was used as the cathode material, but this material produces power densities similar to those obtained with SS mesh [17]. Although a lower buffer concentration of 50 mM was used in this study compared to 100 mM, the maximum power density with the PDMS binder ($1710 \pm 1 \text{ mW m}^{-2}$ with copper mesh) was still higher than the best performance achieved using the neutral hydrophilic binder of 1470 mW m^{-2} [15], and the best result among poly(sulfone) binders of 1660 mW m^{-2} with 100 mM phosphate buffer [14]. The cathodes with PDMS binder had more stable power production than those using a Nafion binder, which was consistent with previous results that non-ionic binders showed more stable performance than Nafion binder [14,15]. Power production at cycle 15 (15 days of operation; average of ca. 1500 mW m^{-2} with SS or copper) remained higher than the best result of 1310 mW m^{-2} at cycle 11 (20 days of operation, 100 mM phosphate buffer) using neutral hydrophilic binders [15]. Completely replacing the Nafion binder with PTFE has been shown to result in a very low power production of 549 mW m^{-2} [13], which was less than one third of power production that obtained here using the PDMS binder (although a brush anode was used in this study, as opposed to a carbon cloth anode). The use of PDMS binder does not require heating, compared to the PTFE binder that needs to be heated to 370°C after application for fusing of the PTFE emulsion particles. Thus the use of PDMS binder is both easily applied, and improves power production over time.

3.2. Coulombic recovery

In general, the different cathodes had similar coulombic recoveries (CRs), which is expected as the cathodes had the same diffusion layers and similar current densities. At cycle 15, copper mesh cathodes with the PDMS binder had only a slightly higher CR of $62 \pm 2\%$, compared to $56 \pm 1\%$ for SS mesh with Nafion binder, $54 \pm 2\%$ for copper mesh with Nafion and $53 \pm 2\%$ for SS mesh with PDMS binder (Fig. 3). The small differences in CR might have resulted from variations in the amount of biofilm that developed over time on cathodes. As the external resistors were set to the resistance where maximum power was obtained, these coulombic recoveries were not obtained at exactly the same current densities, but do indicate the CRs when the MFCs produced maximum power.

3.3. Cathode galvanostatic polarization

Cathodes were examined under abiotic conditions in an electrochemical cell to compare their performance in the absence of bacteria and a substrate. Cathodes with the PDMS binder initially had higher overpotentials than those with Nafion binder at low current densities, which we attributed to insufficient wetting of the cathode surface. When a larger current density was set, oxygen reduction occurred at a higher rate, which would have formed water faster inside the cathode, thus wetting the cathode surface more rapidly at the catalyst sites. This could explain the similar performance of the PDMS cathodes and those with Nafion binder at higher current densities (Fig. 4A). When the galvanostatic polarization tests were repeated one day later, which would have allowed more time for wetting of the hydrophobic PDMS binder, all cathodes showed nearly identical performance at all current densities (Fig. 4B). These results were generally consistent with the MFC tests, where at the first cycle cathodes with Nafion binder showed much higher potentials than PDMS binder, but after six cycles the cathode potentials were very similar to each other.

3.4. Electrochemical impedance spectroscopy

EIS was performed at different cathode potentials of 0.2 V, 0.1 V and 0 V, which were similar to those of the cathodes in MFC tests. Total impedance decreased with increasing oxygen reduction overpotential ($0.2 \text{ V} \rightarrow 0.1 \text{ V} \rightarrow 0 \text{ V}$), as shown by the decrease in the size of the semi-circle produced in Nyquist plots, due to the

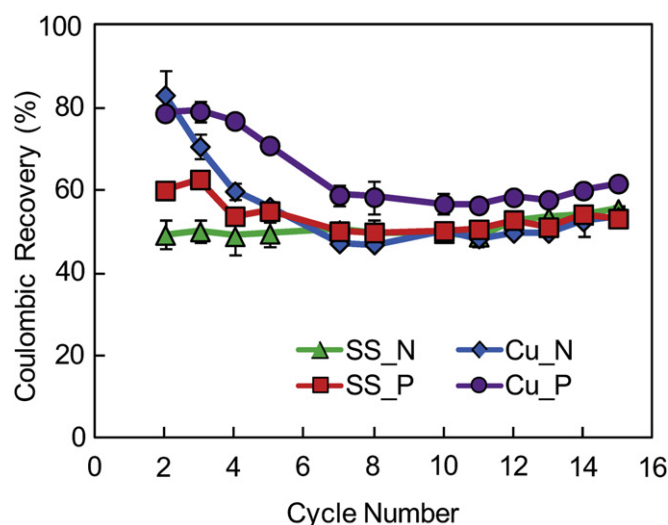


Fig. 3. Coulombic recoveries over cycles with cathodes built around either stainless steel or copper mesh, with PDMS or Nafion binder.

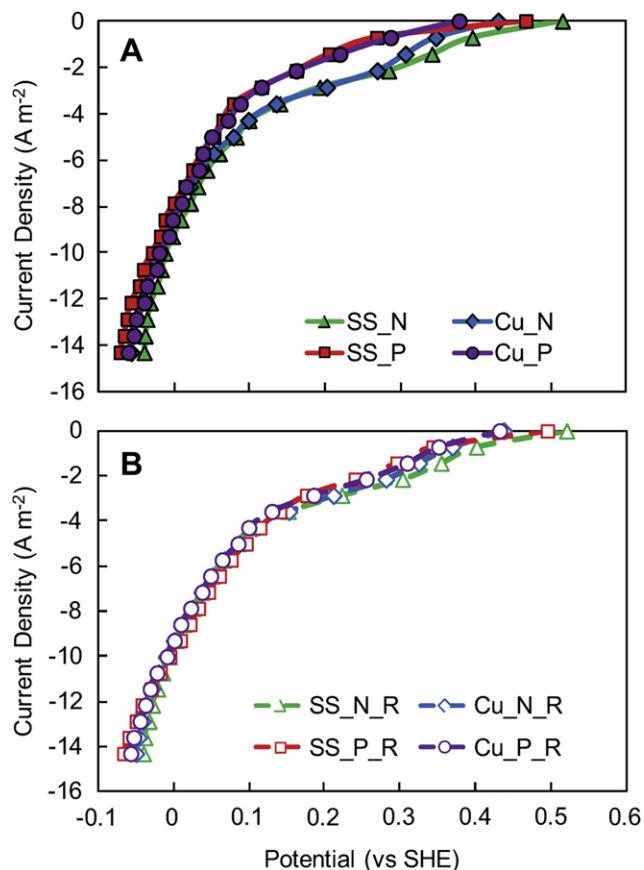


Fig. 4. Galvanostatic polarization of cathodes built around either stainless steel or copper mesh, with PDMS or Nafion binder: (A) immediately after putting cathodes into the reactor; (B) one day after the previous polarization test.

increasing kinetic driving force by larger overpotentials (Fig. 5). At a high potential of 0.2 V (i.e. low overpotential), cathodes with PDMS binder performed similarly to those with Nafion binder. Copper mesh cathodes with Nafion had the smallest total impedance, as shown by the smallest semi-circle in the Nyquist plots. Cathodes with the PDMS binder had smaller total impedance than the cathode with SS mesh and Nafion binder (Fig. 5A). At lower potentials of 0.1 V and 0 V, cathodes with the PDMS binder have less impedance than those with Nafion, as shown by smaller semi-circles in the Nyquist plots (Fig. 5B and C). Copper mesh cathodes had similar EIS spectra to those with SS mesh using PDMS binder, and a smaller impedance than SS mesh with Nafion binder (Fig. 5), consistent with the similar power production with two metal mesh using PDMS binder and higher power production with the copper mesh and Nafion binder.

EIS spectra were fitted to an equivalent circuit to identify the individual components of the cathode internal resistance. Solution resistances (R_s) were similar due to the use of the same cell configurations and solution (Fig. 6). This part of the resistance became dominant at high overpotentials, although this resistance could be reduced by changing the reactor design to have a separator electrode assembly (SEA) setup with closely spaced electrodes [26]. Cathodes with PDMS binder generally had higher charge transfer resistances (R_{ct}) than those with Nafion binder, probably due to the lack of proton conductivity with PDMS. With PDMS binder, copper and SS mesh showed similar R_{ct} , which all decreased with increasing overpotential, with average of 18 Ω at 0.2 V, 10 Ω at 0.1 V and 3.8 Ω at 0 V. With Nafion binder, copper mesh showed smaller R_{ct} than SS mesh at lower overpotentials, due to higher electrical

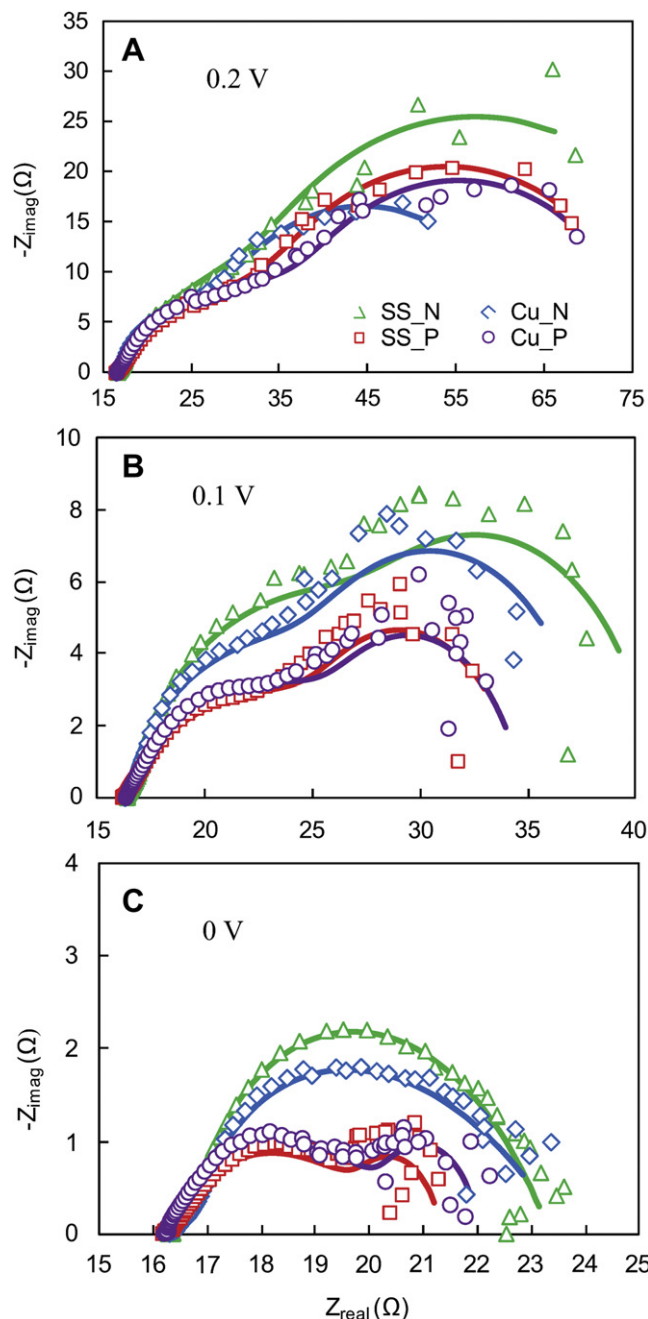


Fig. 5. Nyquist plots of EIS spectra after at different cathode potentials of (A) 0.2 V, (B) 0.1 V, (C) 0 V. Symbols represent experimental data, and lines represent data fit with the equivalent circuit.

conductivity of copper, resulting in the higher power production with copper than SS. Copper mesh had R_{ct} of 12 Ω compared to 15 Ω with SS mesh at 0.2 V, and 9 Ω compared to 13 Ω with SS at 0.1 V. At the highest overpotential of 0 V, copper and SS mesh had similar and much reduced R_{ct} of 0.4 Ω , which was much smaller than the 3.8 Ω obtained with the PDMS binder (Fig. 6).

Cathodes with a PDMS binder had a lower diffusion resistance (R_d) than those with a Nafion binder, which we attributed to the improved anti-flooding properties of the PDMS binder. With the same binder, R_d was similar for the copper and SS mesh, except for cathodes with Nafion binder at 0.2 V. At low overpotentials, where moderate or lower water production would have occurred due to smaller current densities, cathodes with PDMS binder had slightly

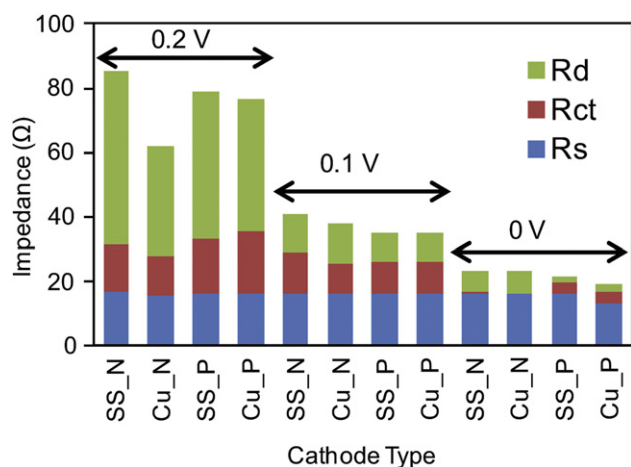


Fig. 6. Component analysis of EIS spectra at different cathode potentials of 0.2 V, 0.1 V and 0 V, with cathodes built around either stainless steel or copper mesh, with PDMS or Nafion binder.

smaller R_{ds} (17–33% less than those with Nafion binder, depending on the potential and metal type). At the highest overpotential (0 V) where current was very large, water production would have been much higher. Under this condition, cathodes with the PDMS binder had much smaller R_{ds} of 1.5 Ω with SS, and 1.9 Ω with copper, compared to 6.7 Ω with SS and 6.9 Ω with copper and the Nafion binder (Fig. 6). Therefore, the total cathode impedance decreased with the PDMS binder, as a result of largely decreased R_d and slightly increased R_{ct} . We attribute the decrease in R_d to be a result of the improved anti-flooding properties of PDMS compared to Nafion. The results here are consistent with previous EIS studies that have shown that the cathode diffusion resistance was larger than the charge transfer resistance of MFC air cathodes [21,27].

3.5. Cathode cost

The cost of the PDMS elastomer kit was \$50 (500 g), which translates to a cost of \$1.5 per m^2 when used as the binder, and is a small cost compared to the other cathode materials. The PDMS cost is also substantially less than that of Nafion (\$667 per m^2 , based on \$200 for 100 mL of 5 wt% solution). Thus the use of PDMS is much more cost-effective than a Nafion binder. The cost of cathode mesh (50 \times 50 SS) was <\$40 per m^2 , based on our purchase of a small piece of material for this study. The bulk price of stainless steel is \$4 per kg, compared to \$8 per kg for copper. Although the cost of copper mesh is higher, the use of this material might be justified in large scale applications where good conductivity may be important for very large cathodes. Although a Pt/C catalyst was used in this study, previous work has shown that this material can be replaced by inexpensive activated carbon that produces only slightly less power densities than Pt [28]. Based on these results, PDMS appears to be a promising binder for MFCs that can improve long-term cathode performance and reduce capital costs.

4. Conclusions

These results have shown that PDMS is a promising low-cost alternative binder to Nafion for MFCs that can achieve comparable power densities and improved stability over time. We attribute these improvements to the anti-flooding and possible anti-

fouling effects of PDMS that resulted from its hydrophobicity. Cathodes with PDMS binder had coulombic recoveries similar to those with a Nafion binder. Electrochemical tests showed that cathodes with PDMS binder had better performance based on reduced impedance, due to a decrease in the diffusion resistance, with only a slight increase in charge transfer resistance. This decrease in diffusion resistance was likely a result of the hydrophobic PDMS preventing the catalyst sites from becoming completely filled with water, which would have improved oxygen mass transfer. This open structure could also have reduced proton conductivity, but apparently this was not an issue with this material. The cost of PDMS is quite low, which is about 0.23% of the cost of using a Nafion binder with these cathodes. PDMS is therefore a very promising low-cost alternative to Nafion as a binder in MFC cathodes, which will make it useful for large scale applications of MFCs.

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